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Occurrence of Extractable Hydrocarbons in Sediments from Raritan Bay, New Jersey

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16. ABSTRACT

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OCCURRENCE OF EXTRACTABLE HYDROCARBONS IN SEDIMENTS FROM RARITAN BAY, NEW JERSEY

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ABSTRACT. *Sediments from 22 sites in the Raritan Bay — Lower New York Bay complex showed that extractable hydrocarbons and percent volatiles increased as the silt-clay content of the sediment increased. The hydrocarbons appeared to be concentrated in the deeper center of Raritan Bay and the Raritan Bay muds, heading down the Bay towards Sandy Hook. Extractable hydrocarbons ranged from 2.2-1098.2 μg/g of dry sediment and the percent volatiles ranged from 0.85-11.39. A peak within the n-C_{18} range and a large "unresolved complex mixture" were characteristic of gas chromatograms. Mixed isomers of benz-pyrene and benz-anthracence and unidentified 1-6 ring polynuclear aromatic hydrocarbons were present.*

INTRODUCTION

Hydrocarbons may enter the estuarine environment by many routes including air pollution fallout, sewage, rivers, dredging and industrial outfalls. The tidal nature of estuaries increases the probability that some hydrocarbons will be retained and deposited. Hydrocarbons present in an ecosystem can frequently be divided into two components: a) those recently derived biogenically from flora, fauna, detritus, and b) those derived from fossil hydrocarbons by anthropomorphic activities or seepage from the earth. Many of the hydrocarbons are potentially dangerous to human health and knowledge of hydrocarbon content and distribution is necessary for management decisions, e.g., dredging impacts, spill treatment effects and alternatives, and use of biotic resources (shellfish).

The Raritan Bay — Lower New York Bay Complex receives hydrocarbons from municipal and industrial wastes, both directly and from tributary waters (Tanacredi, 1977). Unknown amounts of hydrocarbons have entered the bay from oil spills in the Arthur Kill and Raritan River, yacht marinas, ship traffic, and dredging. The Hudson River may also contribute hydrocarbons from the upper New York Bay and New York City environs. DeFalco (1967) reviewed many types and sources of effluents. The circulation patterns (Patten, 1962) and flushing rates in the Raritan Bay — Lower New York Bay Complex tend to retain introduced pollutants.

DeFalco (1967) described general sediment regions of the Bay but particle-size distributions were not reported and extractable hydrocarbons were not quantified with respect to sediment types. Grain-size properties of the sediments may affect the transport and preservation of organic compounds and absolute amounts of sedimentary hydrocarbons considered without other information on the physical properties of the sediments may be of little value (Wehmiller and Lethen, 1975). This study attempted to survey the grain-size distribution, percent volatiles and extractable hydrocarbons of the sediments of the Raritan Bay — Lower New York Bay Complex.

METHODS

Sediments were obtained from the Lower New York Bay — Raritan Bay Complex during June, 1977 (Fig. 1). Samples were not taken near ship channels or dredge spoil areas to avoid overt possibilities of contamination. Benthic surface sediments were sampled with a Petersen Grab (0.1 m^3). Several grabs were taken per station and composited. Sediments for chemical analysis

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ERRATA: The illustrations for Figures 2 and 4 have been switched. The chromatograms depicted in Figure 2 should have the legend of Figure 4, and the chromatograms of Figure 4 should have the legend of Figure 2.

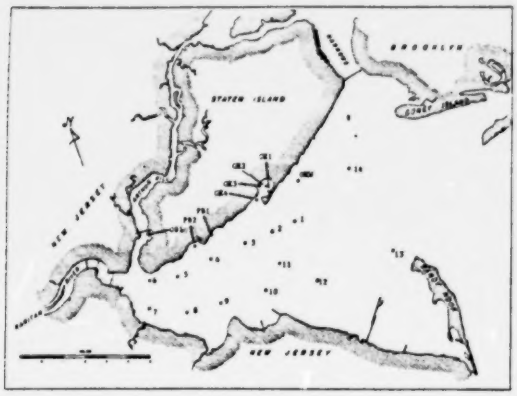

FIGURE 1. Location of sampling sites. Intertidal samples were taken at OB1 (near the Outerbridge Crossing), PB1 (Sequine Point), GK4 (a sand bar at the mouth of Great Kills Harbor) and GK3 (below a storm sewer outfalk). Sub-littoral samples were taken at stations 1-14, GK1 and GK2 (in Great Kills Harbor), PB2 (Princes Bay) and OKWD (off the outfall of the Oakwood Sewerage Treatment Plant.

were placed in quart mason jars with tin lined caps, refrigerated at 4°C, and analyzed within two months. All collection and storage materials were washed with "distilled in glass" hexane (Burdick and Jackson, Muskegon, Mich.). Sediments for textural characterization were subsampled from the grab composite. Similar procedures were utilized in the analysis of littoral samples.

Particle-size analyses were performed by sieving 100 g dry weight of sediment through a series of U.S. Standard Wire-cloth sieves (4 mm, 2 mm, 0.5 mm, 0.24 mm, 0.125 mm, and 0.063 mm). Macrodebris (i.e., shells, large rocks) were excluded from samples prior to weighing. Dried congealed sediments (mud) were ground with a mortar and pestle prior to sieving. The sediments were sieved for 30-40 minutes. Sediment fractions were then weighed and relative percentages were calculated.

Percent volatiles of the sediments were measured by placing predried sediment samples in a muffle furnace at 500-800°C for 24 hours. Differences in weight were calculated as percent volatiles. Total extractable hydrocarbons were analyzed using a modification of the method of Giger and others (1974). All material was prewashed with Freon 113 prior to use. Approximately 50 g of sediment from each sample was dried to constant weight at 60°C for two days. Sediments were then transferred to 250 ml screw top Erlenmeyer flasks (sand sediments were separated with a spatula, mud sediments were ground in an agate mortar). Fifty ml of Freon 113 was added to each flask. Flasks were sealed with a tinfoil lined cap and tumbled 10 minutes on a wrist action shaker. The freon extract was then filtered through glass wool into a 100 ml volumetric flask. An additional 50 ml of freon was added to the sediment in the Erlenmeyer flasks and tumbled for another 10 minutes. This supernatant was then filtered through glass wool and added to the first. The combined extracts of each sample were brought to volume and dried with anhydrous sodium sulfate previously baked at 150°C to remove impurities. The extracts were analyzed by Infrared Spectroscopy utilizing 10 and 1 cm cells in a Perkin-Elmer Model 457 Infrared Spectrophotometer. The extracts were scanned from 3200 cm^{-1} to 2700 cm^{-1} and quantitated at 2930 cm^{-1} (Gruenfeld, 1973). Subsamples (25 ml) of selected extracts were analyzed by gas chromatography and fluorescence spectroscopy.

The remaining freon extract in each flask was treated with 2 g of 2% deactivated silica gel to remove non-hydrocarbon interferences (Gruenfeld and Frederick, 1977). The treated extracts were then re-analyzed by IR Spectroscopy similar to the pretreated samples. All extracts were quantitated by comparing the absorbances to a reference mixture of iso-octane and hexadecane in freon. To determine the types of hydrocarbons present and the effects of silica gel treatment, select samples from oil contaminated sites (GK3 and OB1) were analyzed by gas chromatography.

For gas chromatographic analysis, samples were dried under carbon filtered air and brought to 100 µl volume with cyclohexane (Fisher 99 Mol %). A Perkin-Elmer (Model 900) gas chromatograph was used, equipped with a flame ionization detector and a six foot stainless steel column packed with 3% OV-1 on 80/100 mesh of Chromosorb WAW. Operating conditions

TABLE 1. Particle size classification (percent retained on sieves), percent volatiles, and extractable hydrocarbons before (BT) and after (AT) silica gel treatment (μg/g dry sediment).

Sampling site	Particle size (Wentworth)								Extractable hydrocarbons	
	Granules	Very coarse sand	Coarse sand	Medium sand	Fine sand	Very fine sand	Silt-clay	Percent volatiles	(BT)	(AT)
1	0.9	3.5	20.8	66.6	6.8	1.1	0.2	1.35	18.4	11.5
2	2.4	2.0	3.1	14.6	39.0	34.2	4.1	3.06	292.3	269.2
3	0.0	0.2	0.4	1.1	4.9	65.3	27.6	5.53	422.5	395.7
4	0.4	0.7	1.4	1.9	4.0	55.9	33.9	8.55	840.0	768.3
5	0.6	2.1	4.4	5.3	12.5	42.7	30.4	11.39	444.9	414.3
6	19.9	14.0	19.7	31.4	13.8	0.6	0.3	0.85	74.8	55.1
7	3.3	4.2	6.0	20.9	24.2	24.7	14.7	3.80	179.3	179.3
8	2.3	3.7	10.4	16.5	13.4	32.7	20.4	5.12	120.0	120.0
9	1.2	3.5	5.5	13.8	24.8	27.7	22.7	5.41	696.8	636.7
10	0.0	0.2	0.7	2.3	26.3	10.0	59.8	7.36	329.5	307.2
11	8.0	7.4	8.8	33.1	17.9	12.8	11.4	3.79	441.0	412.9
12	0.0	1.0	2.7	5.2	10.0	28.7	52.2	8.84	572.0	549.5
13	0.2	1.2	2.7	4.4	52.4	23.2	14.7	5.41	381.4	332.9
14	1.3	1.1	2.4	10.3	36.9	43.4	4.5	1.47	34.8	30.4
GK 1	0.1	0.7	2.5	4.3	10.0	31.9	50.1	7.02	672.6	655.6
GK 2	0.1	0.1	0.4	1.1	21.0	42.5	34.1	7.38	1194.3	1098.2
GK 3	13.7	8.5	16.4	29.7	21.9	6.2	3.5	2.56	715.2	590.2
GK 4	8.0	15.6	36.0	38.4	1.4	0.3	0.2	0.35	7.2	2.2
PB 1	4.5	2.6	5.0	36.6	48.0	2.9	0.4	0.95	14.5	9.6
PB 2	4.8	4.9	9.5	39.6	33.4	5.0	2.8	1.31	109.4	98.3
OB 1	21.7	7.8	16.9	42.8	8.2	1.3	1.0	2.8	737.8	641.3
OKWD	12.8	6.9	16.1	42.3	19.8	1.8	0.3	0.91	19.9	16.6

were: carrier gas; He_2; column temperature; 60°C with a two-minute hold, programmed to increase 8°C/minute to 300°C; injection sample: 1-2 microliters. Sample peak areas were identified by matching to alkane standards.

Sample volumes were then diluted to 5 ml with cyclohexane and analyzed for polynuclear aromatic hydrocarbons (PNA) by synchronous excitation fluorescence spectroscopy (Frank, 1978). Confirmation was obtained by combination HPLC and fluorescence spectroscopy. An ODS reverse phase column (DuPont) and a mobile phase of 50:50 2-propanol/water was used to chromatograph the sample. The predominant constituent was isolated and collected. Both single wavelength (emission) and synchronous excitation spectra were then obtained by fluorescence analysis in a 10 mcl cuvette. Solutions of known PNA standards were similarly analyzed. Retention times on chromatograms and fluorescence spectra were used as identification parameters for the chromatographed sample constituent.

RESULTS

The results of textural analysis, determination of percent volatiles and quantitation of extractable hydrocarbons are presented in Table 1. Values of hydrocarbons are reported before and after silica gel treatment to illustrate the large residual amount of hydrocarbons remaining after treatment. Silica gel treatment removed an average of 14.4% of non-hydrocarbon material from extracts. The extractable hydrocarbons (after silica gel treatment) ranged from 2.2 to 1098.2 mg/g of dry sediment.

Percent volatiles and μg extractable hydrocarbons (after silica gel treatment) were examined to relate their quantitative values to the percent silt-clay fraction of the sediment. Table 2 indicates that the percent volatiles and μg extractable hydrocarbons apparently increase as the silt-clay fraction increases.

Relationships between the silt-clay fraction, percent volatiles and μg of extractable hydrocarbons were analyzed by linear regression. A cor-

TABLE 2. The percent volatiles and μg extractable hydrocarbons (recorded as mean values ± S.E.) determined sediments with different silt-clay fractions.

% Silt-clay fraction	n	% Volatiles	μg extractable hydrocarbons
0.1- 1.0	5	0.88 ± 0.16	19.0 ± 9.31
1.1-10.0	4	2.1 ± 0.42	247.0 ± 124.9
10.1-20.0	3	4.3 ± 0.54	308.4 ± 68.2
20.1-30.0	3	5.3 ± 0.13	384.1 ± 149.3
30.1-40.0	2	10.0 ± 1.42	591.3 ± 177.0
40.1-50.0	0		
50.1-60.0	3	7.7 ± 0.56	504.1 ± 103.1

relation coefficient of 0.64 was found for the regression of the percent silt-clay fraction vs. μg of hydrocarbons. A correlation coefficient of 0.73 was calculated for the regression of the percent volatiles vs. μg of hydrocarbons. However, the calculated standard error of the regression for both of the above indicated considerable scatter around both calculated regression lines. The calculated correlation coefficient (0.85) of the regression between the silt-clay fraction and the percent volatiles indicated a closer relationship. In calculations, data from sites OB1 and GK2 were excluded because of several previous spill events of petroleum oil (OB1) and sewage (GK2).

To determine types of hydrocarbons present and the effects of silica gel treatment, select samples (OB1, GK3, Sites 1, 4, 5, 6, 8, 11 and 12) were analyzed by gas chromatography. Figure 2 illustrates chromatograms of samples from sites OB1 and GK3, before and after silica gel treatment. Although some material was removed by the silica gel, the occurrence of a large "unresolved complex mixture" in the chromatograms indicated the hydrocarbon material was not recently biologically produced (Gruenfeld and Frank, 1977). The chromatogram of site OB1 illustrates residual oils in the sediment after several spill incidents of crude and fuel oils over a period of years. The chromatograms of GK3 indicate the presence of well weathered oil, higher boiling materials and possible sewage derived hydrocarbons from the storm sewer outfall which was located approximately 40 feet from the site. Gas chromatograms of a light Arabian Crude oil and a No. 2 fuel oil are presented in Figure 3 to illustrate non-weathered oil chromatograms.

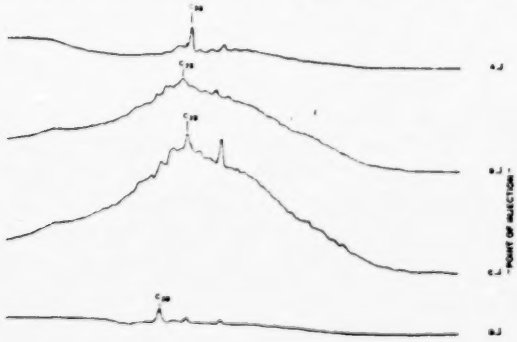

FIGURE 2. Gas chromatograms of Sites OB1 (A) and GK3 (C). Chromatograms B and D are sites OB1 and GK3 after treatment with silica gel. The baseline is drawn below chromatogram D.

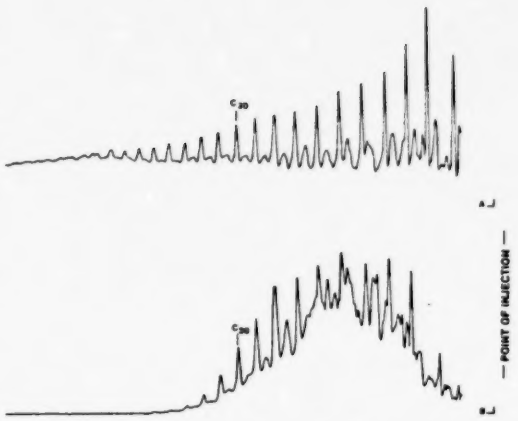

FIGURE 3. Gas chromatograms of Light Arabian Crude oil (A) and No. 2 fuel oil (B).

Figure 4 contains chromatograms from Sites 1, 4, 5 and 6. A large indigenous hydrocarbon content is evident in the chromatograms of Sites 4 and 5. Site 4 was near the "Raritan Bay-West Reach Ship Channel" and the Site 5 sample was from a large mud bank. Sites 1 and 6 were sandy areas and the chromatograms indicate low levels of hydrocarbons present.

Synchronous fluorescence spectra were obtained for samples from Site OB1 and GK3 (before silica gel treatment; (Frank, 1977) and Sites 1, 5, 6 and 8. In analyzing the spectra of OB1 and GK3, benz-pyrene (mixed isomers) were the predominant compounds with possible

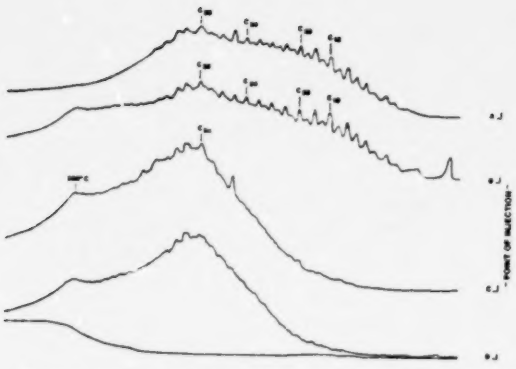

FIGURE 4. Gas chromatograms of Site 1 (A), Site 4 (B), Site 5 (C) and Site 6 (D).

4 and 6 ring compounds present. In the Site 1 spectra, two ring compounds were the most prevalent (with possible three ring compounds present), five ring compounds exhibited a well resolved peak and a six ring compound peak was partially resolved. In the Site 5 spectra, benz-anthracence was predominant with benz-pyrene and other five ring compounds prevalent. The peaks for benz-anthracence and benz-pyrene were well resolved. In the spectra of Site 6, three ring compounds were prevalent, probably anthracence. Five ring compounds were next in prevalence with six ring compounds indicated in the spectra. The spectra of Site 8 indicated a predominance of three ring compounds with 5 and 6 ring compounds present and partially resolved.

DISCUSSION

The particle-size distributions found in this study generally conformed to those found by DeFalco (1967). This indicates that the general bottom sediment distribution is a relatively stable feature of the Bay.

The particle-size distribution and percent volatiles reported here indicates a pattern of movement of sediments in the Bay complex. The sediments entering the Bay from various locations move progressively toward the area bounded by Sequine Point, Great Kills, Keyport and Keansburg. The pattern conforms with earlier descriptions by DeFalco (1967) and Greig and McGrath (1977). The distribution of extractable hydrocarbons reflects this sediment movement with relatively high values at Stations 4, 5, 7, 8, 9, 10 and 11. Generally, sample sites with high percent volatiles were areas with large silt-clay and fine-sand fractions.

Several of the values of μg of extractable hydrocarbons after treatment were higher than others and reflect the area sampled. Site GK2 was sampled from the center of Great Kills Harbor and receives inputs of petroleum hydrocarbons from boat marinas, storm sewers and dredging. Sites GK1 and GK3 also contain hydrocarbons found within semi-enclosed Great Kills Harbor. The hydrocarbon material found at Site OB1 reflects several previous oil spills within the Arthur Kill. This beach was predominantly medium and coarser sands, and oil appeared in bootprints while sampling. When taking sediments, a light crude or fuel type oil appeared at the bottom of the hole. Site 4 was near the "Raritan Bay-West Reach Ship Channel" and the higher hydrocarbon values may reflect settled dredge spoil or ship derived hydrocarbons.

Gas chromatograms frequently exhibited a large 'unresolved complex mixture' indicative of pollution derived hydrocarbons. The Bay receives large amounts of sewage from many sources, and both Hatcher and others (1977), and Goodfellow and others (1977), have reported frequent contamination of sediments by sewage derived coprostanol (an n-C_{28} sterol). Some material eluting in the chromatographs in this study in the n-C_{28} region may also be sewage derived contaminants. However, Wehmiller and Lethen (1975) reported that Delaware estuary sediments showed a significant 'unresolved complex mixture,' and many chromatograms also contained a mixture that peaked in the n-C_{28} to n-C_{30} region. They termed these "high boiling" mixtures which were frequently observed in coarse grained sediments.

The lack of resolution in the chromatograms of this report indicates that a substantial amount of hydrocarbon material is present. The fluorescence spectra indicated that many aromatic compounds were present. Mixed isomers of both benz-pyrene and benz-anthracene were frequently found with other 1-6 ring compounds present.

Hites and others (1977), and Tanacredi (1977), have also reported the occurrence of PNA hydrocarbons in sediments. Although Tanacredi reported that sewers in Jamaica Bay were discharging PNA hydrocarbons, the derivation of aromatic hydrocarbons in this study is not known.

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THE INFLUENCE OF MAGNETIC VARIATIONS ON ATMOSPHERIC ION CONCENTRATION AND TEMPERATURE

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Abstract. *The amount of change in the atmospheric ion concentration due to either (a) variations in the earth's dipole moment which occur on a time scale of the order of 10,000 years, or (b) geomagnetic storms produced by the extraterrestrial ring current with a time scale of a few days, is estimated. The variation in the earth's dipole moment over the past 10,000 years produces ± 25% change in the atmospheric ion concentration, with high values of the dipole moment corresponding to low ion concentrations and vice versa. Geomagnetic storms which are produced primarily by the extraterrestrial ring current and result in a reduction of the earth's effective dipole moment can increase the ion concentration by 25% for a large (500 gamma Dst)*

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